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(21) International Application Number: PCT/US94/08263 (22) International Filing Date: 22 July 1994 (22.07.94) (30) Priority Data: 08/099,676 29 July 1993 (29.07.93) US (71) Applicant: ALLIEDSIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US). (72) Inventors: VAN DER PUY, Michael; 32 Joanne Lane, Cheektowaga, NY 14227 (US). EIBECK, Richard, Elmer; 23 Pine Terrace, Orchard Park, NY 14127 (US). ELLIS, Lois, Anne, Shorts; 35 James Place, Orchard Park, NY 14127 (US). MADHAVAN, Gajavalli, Venkatrao, Bindu; 99 Kings View Road, Amherst, NY 14221 (US). (74) Agent: CRISS, Roger, H.; AlliedSignal Inc., Law Dept. (C.A. McNally), 101 Columbia Road, P.O. Box 2245R, Morristown, NJ 07962-2245 (US).		(81) Designated States: CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
(54) Title: PROCESS FOR THE PREPARATION OF 1,1,1,3,3-PENTAFLUOROPROPANE (57) Abstract <p>This invention is related to the preparation of hydrofluorocarbons (HFCs). Specifically, it relates to the manufacture of 1,1,1,3,3-pentafluoropropane, $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ (HFC-245fa) by the steps comprising (1) the formation of $\text{CCl}_3\text{CH}_2\text{CCl}_3$ by the reaction of CCl_4 with vinylidene chloride; (2) the conversion of $\text{CCl}_3\text{CH}_2\text{CCl}_3$ to $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ by reaction with HF in the presence of a fluorination catalyst, selected from TiCl_4, SnCl_4 or mixtures thereof; and (3) reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ to $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$.</p>		

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PROCESS FOR THE PREPARATION OF 1,1,1,3,3
PENTAFLUOROPROPANE

BACKGROUND OF INVENTION

10 This invention is related to the preparation of hydrofluorocarbons (HFCs). Specifically, it relates to the manufacture of 1,1,1,3,3-pentafluoropropane, $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$, which is referred to in the art as HFC-245fa.

15 HFCs are of current interest due to their potential to replace ozone depleting CFCs and HCFCs which are used in a variety of applications including refrigerants, propellants, blowing agents, and solvents. The compound $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ has physical properties, including a boiling point of
20 about 14°C , which makes it particularly attractive as a blowing agent or propellant. Its ability to function in a manner similar to CFC-11 (CCl_3F , bp 24°C), a well known aerosol propellant at the time, was noted by Smith and Woolf in U.S. Patent 2,942,036 (1960). Ger. Offen, DE 3,903,336, 1990 (EP 381 986 A) also states (using a generic formula) that $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ may
25 be used as a propellant or blowing agent. The use of HFC-245fa as a heat transfer agent is also mentioned in Jpn. Kokai Tokyo Koho JP 02,272,086 (Chem. Abstr. 1991, 114, 125031q).

30 1,1,1,3,3-Pentafluoropropane was first made by the reduction of $\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$ over a palladium catalyst (Smith and Woolf, U.S. Patent 2,942,036, 1960). Materials exiting the reaction zone including $\text{CF}_3\text{CH}_2\text{CHF}_2$, $\text{CF}_3\text{CH}=\text{CF}_2$, $\text{CF}_3\text{CCl}=\text{CF}_2$, and unreacted starting material. The desired $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$ was formed in yields up to about 60%, but the source of the starting material was not disclosed. Reduction of 1,1,1,3,3-pentafluoropropene was disclosed by Knunyants et al. (Chem. Abstr., 1961,
35 55, 349f). The yield of pentafluoropropane was 70%. The only other preparation of $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$ we are aware of, is its formation, in low yield,

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during the elemental fluorination of tetrahydrofuran (Burdon et al., J. Chem.
5 Soc., C, 1969, 1739).

It is the object of this invention to provide a means of manufacturing
1,1,1,3,3-pentafluoropropane which is economical and amenable to large
scale, using readily available raw materials. The process of this invention
10 involves three basic steps, of which any step or combination thereof is
novel in the art.

The three steps of the process of this invention are as follows:

15 1) the formation of $\text{CCl}_3\text{CH}_2\text{CCl}_3$ by the reaction of CCl_4 with
vinylidene chloride;

2) the conversion of $\text{CCl}_3\text{CH}_2\text{CCl}_3$ to $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ by reaction with
HF in the presence of a fluorination catalyst, selected from TiCl_4 , SnCl_4 or
20 mixtures thereof ; and

3) reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ to $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$.

Each step is conducted under process conditions ,i.e. temperature and
25 pressure, sufficient to produce the desired product as discussed herein.

DETAILED DESCRIPTION

The telomerization of vinylidene chloride by reaction with CCl_4 is
30 known in the art and has been studied in some detail. The telomerization
reaction produces compounds of the formula $\text{CCl}_3(\text{CH}_2\text{Cl})_n\text{Cl}$, where n
varies as needed for the products desired. The telomerization of vinylidene
chloride can be initiated by several means, but initiation with metal salts,
particularly of copper, has distinct advantages for the process of this
35 invention. The copper salts are believed to initiate the reaction by first
reacting with CCl_4 to produce a trichloromethyl radical which then
combines with vinylidene chloride, initiating the telomerization (see for

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example, Assher and Vofsi, J. Chem. Soc., 1961, 2261 for a discussion of
5 the mechanism). The copper salts also terminate the telomerization by
chlorine atom transfer to the growing radical chain. Thus, the chain lengths
are shortened considerably, compared to e.g. peroxide initiated
telomerizations. For the reactions of interest here, telomers having 3 to 9
carbon atoms are obtained in excellent yield. Some control of the telomer
10 distribution is feasible by controlling the reaction conditions, notably the
ratio of CCl_4 to vinylidene chloride and the type of copper salt used (see for
example Belbachir et al., Makromol. Chem. 1984, 185, 1583-1595). Thus
it is possible to obtain $\text{CCl}_3\text{CH}_2\text{CCl}_3$ with very little higher molecular weight
telomers (see Example 1).

15 A variety of catalysts have been used in telomerization processes.
To a large degree, many of these telomerization catalysts, including
mixtures thereof, can be equivalent, and the choice of catalyst depends on
cost, availability, and solubility in the reaction medium. For the
20 telomerization reaction of this invention, it was discovered that salts of
copper and iron are preferred. Overall, for the reaction of interest here, the
more preferred catalysts are cuprous chloride, cupric chloride, or mixtures
of the two or cuprous iodide. The amount of catalysts used in the
telomerization reaction is at least about 0.1 mmol, and preferably, about
25 0.1 to about 50 mmol, per mole of saturated halogenated hydrocarbon
(e.g., CCl_4 or $\text{CCl}_3\text{CH}_2\text{CCl}_3$) used. At very low concentrations, the reaction
rate may be unacceptably slow, and very high catalyst concentrations may
be wasteful due to the fact that the solubility limit may have been reached
at even lower catalyst to CCl_4 ratios. Consequently, the more preferred
30 amount of catalyst is about 1 to 20 mmol, per mole of saturated
halogenated hydrocarbon.

It is also noted that a co-catalyst can be used in the telomerization
process. Amines may be employed as co-catalysts, preferably in
35 concentration of 1 to 10 moles per mole of metal catalyst (i.e. copper salt).
Such amine co-catalysts include alkanol amines, alkyl amines and aromatic

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amines, for example ethanolamine, butyl amine, propyl amine, benzylamine, pyridine and the like.

The ratio of CCl_4 to vinylidene reactant will substantially alter the degree of polymerization, i.e. average value of n for compounds of the formula $\text{CCl}_3(\text{CH}_2\text{Cl})_n\text{Cl}$. Thus, for example, if the desired product has only one more $-\text{CH}_2\text{CCl}_2-$ unit than the starting material, the ratio of CCl_4 (or $\text{CCl}_3\text{CH}_2\text{CCl}_3$) to vinylidene chloride should be relatively high (at least about 2, and preferably, about 2 to 5), so that higher molecular weight telomers are minimized. If the desired product has two or more $-\text{CH}_2\text{CCl}_2-$ units than the starting material (e.g. $\text{CCl}_3(\text{CH}_2\text{CCl}_2)_2\text{Cl}$ from CCl_4), smaller ratios of CCl_4 to vinylidene chloride (about 0.3 to 1) should be used. The same rationale is used for a system employing vinylidene fluoride.

Useful temperatures for the telomerization reaction range from about 25 to about 225°C , preferably 80 to about 170°C , so that, depending on reactant concentrations and catalyst activity, convenient reaction times will vary from a few hours to about one day. More preferred temperatures are in the 125 to 140°C range.

Finally a variety of solvents can be used. Any solvent which is inert to the reactants and the desired product can be used. Illustrative of such are acetonitrile, dimethylsulfoxide, dimethylformamide, tetrahydrofuran, isopropanol, and tertiary butanol. We prefer acetonitrile due to its low cost, stability, easy recovery via distillation, and ability to dissolve sufficient amounts of inorganic catalyst salts. Primarily for the latter consideration, the amount of solvent is preferably from about one fourth to two thirds of the total volume, and more preferably one third to one half of the total volume. Otherwise, the amount of dissolved catalyst may be relatively low, or the output of product per run will be adversely affected due to a dilution effect.

In the second step, $\text{CCl}_3\text{CH}_2\text{CCl}_3$ is fluorinated to provide $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$. Previously, $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ has been prepared, along with $\text{CF}_2\text{ClCH}_2\text{CF}_2\text{Cl}$, by fluorination of $\text{CCl}_3\text{CH}_2\text{CF}_2\text{Cl}$ with antimony halides

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(Chem. Abstr., 1981, 94:174184u). This method, however, is unsuitable for large scale manufacture due to the cost of the fluorinating agent. The preparation of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ by the BF_3 -catalyzed addition of HF to $\text{CF}_3\text{CH}=\text{CFCl}$ is also known (R.C. Arnold, U.S. Patent 2,560,838; 1951),
5 but the source of $\text{CF}_3\text{CH}=\text{CFCl}$ was not disclosed. We have also found that HF alone or gave relatively low yields of the desired $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$.

Surprisingly, fluorination (of $\text{CCl}_3\text{CH}_2\text{CCl}_3$) with HF in the presence of either TiCl_4 , or SnCl_4 as catalysts can provide the desired $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ in
10 synthetically useful yield. Due to the temperature required for this reaction about (75 to 175°C, and, more preferably, 115 to 135°C,) the reactions are conducted under pressure. The pressure may be controlled by release of by-product HCl, during the reaction process in order to provide a margin of safety if needed depending on the limitations of the equipment being
15 used. We have found it convenient to operate at pressures of about 150 to 500 psig. The upper limit for pressure is generally a limitation of the available equipment. The reactor consisted of a stirred autoclave fitted with a packed column attached to a condenser maintained at 0 to -20°C. Excess pressure (HCl) is vented through a valve at the top of the condenser into a
20 scrubber. At the end of the heating period, the product and remaining HF are vented through a valve on the autoclave head, which in turn is connected to an acid scrubber and cold traps to collect the product. Under fluorinated materials, such as $\text{CF}_2\text{ClCH}_2\text{CF}_2\text{Cl}$ may be recycled along with $\text{CCl}_3\text{CH}_2\text{CCl}_3$ in subsequent batch runs.

25

While both TiCl_4 and SnCl_4 gave similar yields of the desired $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$, TiCl_4 is preferred due to its lower cost, lower toxicity, and availability in bulk.

30

The mole ratio of HF to organic should be about 4/1 to about 20/1, preferably 5/1 to about 9/1. Since over-fluorinated material, $\text{CF}_3\text{CH}_2\text{CF}_3$, is generally not desired, it is more advantageous to allow more under-fluorinated material (which can be recycled) in the crude product. Over-fluorinated product is kept low by smaller HF/organic ratios and lower

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reaction temperatures. The reaction temperatures range from 75 to about 150°C, while the preferred temperatures range from about 115 to about 135°C. Under these conditions, the reaction times range from about one to about 25 hours, and can be monitored by the rate of pressure (HCl) increase.

In the last step, $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ is reduced to 1,1,1,3,3-pentafluoropropane, which is unknown in the art. The reduction can be conveniently accomplished in a continuous flow system by passing vapors of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$, along with hydrogen, over a catalyst.

The latter include nickel, palladium, platinum and rhodium, which are usually supported on inert materials, such as carbon or alumina. These catalysts are available commercially and generally can be obtained having 0.5 to 20% by weight of the metal on the support material. More commonly, loadings of 0.5 to 5% weight percent are employed. Examples include 1% palladium on activated carbon granules and 0.5 % platinum on 1/8" alumina pellets. The more preferred catalyst is palladium due to its lower cost compared to either platinum or rhodium.

While it is most convenient to operate to atmospheric pressure, this is not required. Both subatmospheric pressures or pressures up to 100 atmospheres may be used, the latter especially in batch operations.

In the fluorination step it may be preferable to utilize a solvent, such as methanol, ethanol and acetic acid. A base may also be beneficial to neutralize the HCl produced. Any neutralizing agent can be used, e.g. sodium hydroxide, potassium hydroxide, sodium acetate and sodium carbonate.

Useful temperatures for vapor phase reductions range from about 100 to 350°C, more preferred ranges are 150 to 250°C.

Based on reaction stoichiometry, the required ratio of hydrogen to organic is 1 mole of organic is 1 mole of hydrogen per mole of organic.

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From 1 to about 50 times the stoichiometric ratio may be used. A ratio of 2 to 30 times the stoichiometric amounts can be used with satisfactory results.

The most desirable conditions for the reduction will vary and will depend, in part, on the activity of the catalyst (which depends on the type of metal used, its concentration on the support material, and the nature of the support material), and the contact or residence time in the reactor. Residence times may be adjusted by changing the reaction temperature, the catalyst volume, and the flow rates of hydrogen and/or organic material to be reduced. Useful contact times range from about 0.1 sec to about 2 minutes. In the present case, more preferred contact times range from about 10 to 40 seconds at 200-225°C and atmospheric pressure.

In the reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ at atmospheric pressure and at temperatures of about 100 to 325°C, both $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ and $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ are generally present in the reactor effluent stream. The ratio of $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ to $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ increases with increasing reaction temperature. Continuous operation at high temperatures (> 250°C) is not very advantageous, due to potential gradual loss of the original catalyst activity. Consequently, the preferred method to achieve relatively high conversions of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ to $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ is to increase the contact time, or equivalently, to recycle the product stream until the desired conversion is obtained. After separating the desired $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ from $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$, the $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ may be fed into the reactor again.

30 Example 1 - Preparation of $\text{CCl}_3\text{CH}_2\text{CCl}_3$

A teflon-lined, magnetically stirred autoclave (575 mL capacity) was charged with 150 mL CCl_4 , 150 mL CH_3CN , 0.51 g CuCl and 0.51 g CuCl_2 dihydrate. The autoclave was closed and evacuated briefly. Vinylidene chloride (57.7g, 0.595 mol) was added via syringe and a rubber septum over a ball valve on the autoclave. The autoclave was then pressurized with nitrogen to 20 psig at room temperature. The mixture was heated

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over 1.75 h to 150°C and maintained at 150°C for 2 h. The stirrer speed
5 was maintained at 350 rpm. After cooling the autoclave and contents to
about 15°C, the contents were removed, diluted with 400 mL water, and
the organic layer separated. The aqueous layer was extracted with 50 mL
methylene chloride, and the combined organic layers washed with 100 mL
brine. After drying (Na_2SO_4), the organic layer was concentrated by rotary
10 evaporation to give 140.4 g crude product. Distillation at 2.7 mm Hg gave
114.3g $\text{CCl}_3\text{CH}_2\text{CCl}_3$, bp 63-65°C (77% yield based on vinylidene chloride
added). Its purity by GC analysis was 99.97%. ^1H NMR (CDCl_3): singlet
at 4.17 δ .

15 **EXAMPLE 2 HF Fluorination with TiCl_4**

A 600 mL, magnetically stirred, model autoclave fitted with a
condenser (maintained at -10°C), was evacuated, cooled to about -40°C,
and charged with .6.9 g (0.036 mol) TiCl_4 followed by 64 g (0.255 mol)
20 $\text{CCl}_3\text{CH}_2\text{CCl}_3$, and 102.5 g (5 mol) HF. The temperature was increased to
120°C and maintained at that temperature for a total of 22 h. During the
heating period, pressure in excess of 400 psig was periodically vented to an
aqueous KOH scrubber which was attached to two -78°C cold traps. At the
end of the heating period, the remainder of the autoclave contents were
25 slowly vented. The cold traps contained 36.1g material which by GC
analysis, contained 14.5% $\text{CF}_3\text{CH}_2\text{CF}_3$ and 84.0% $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$,
corresponding to a yield for $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ of 69%.

30 **EXAMPLE 3 - HF Fluorination with SnCl_4**

In the manner and apparatus described in Example 2, 63.5 g
 $\text{CCl}_3\text{CH}_2\text{CCl}_3$, 101.4 g HF, and 13.5 g (0.052 mol) SnCl_4 were heated to
125°C for 23.5 h. The cold trap contained 41.5 g material, which by GC
35 analysis contained 13.4% $\text{CF}_3\text{CH}_2\text{CF}_3$, 66.3% $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$, and 20.3%
 $\text{CF}_3\text{CH}_2\text{CFCl}_2$, corresponding to a yield for $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ of 65%. The crude
products from Examples 3 and 4 were combined and distilled to give 99.4%

pure (GC) $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$, bp 27-30°C. ^1H NMR (CDCl_3): δ 3.2 tq ($J = 9$ and 12 Hz).

EXAMPLE 4 - Reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ - at 200°C

The reactor used in this Example consisted of an electrically heated glass column containing a catalyst bed comprised of a mixture of 10 cc 1% Pd on activated carbon (4-8 mesh) and 15 cc glass helices. Hydrogen was passed over the catalyst at 140 cc/min and $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ was introduced at a rate of 2.25 g/h. The reaction temperature was 200°C. The material exiting the reactor was collected in a cold trap and consisted of approximately 1/3 $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ and 2/3 unreacted $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ by GC analysis.

EXAMPLE 5 - Reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ at 225°C

Example 4 was repeated, except that the reaction temperature was increased to 225°C. The volatile material which collected in the cold trap consisted, by GC analysis, of 51% $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$. The remainder was primarily unreacted $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$. Distillation gave $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$, bp 14°C. the recovered $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ was recycled to provide additional $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$.

EXAMPLE 6 - Reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ at room temperature

An autoclave was charged with a solution of 10 g KOH in 60 mL methanol, 0.5 g 1% Pd on carbon, and 25 g (0.15 mol) $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$. Stirring was begun and the autoclave pressurized to 250 psig with hydrogen. After 20 hours, the contents were cooled to 0°C and excess hydrogen was bled off. The remaining volatile organic material was then transferred to a cold receiver under vacuum. Distillation of the crude material so obtained gave $\text{CF}_3\text{CH}_2\text{CHF}_2$.

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What is Claimed is:

1. A process for the preparation of 1,1,1,3,3-pentafluoropropane ($\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$) comprising:
reacting $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ with hydrogen in the presence of reduction catalyst.
 2. The process of claim 1 wherein the reduction catalyst is selected from nickel, palladium, platinum and rhodium.
 3. The process of claim 1 wherein the $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ is prepared by the step comprising reacting $\text{CCl}_3\text{CH}_2\text{CCl}_3$ with HF.
 4. The process of claim 3 further comprising the step of recycling materials produced other than $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$.
 5. The process of claim 3 wherein the fluorination catalyst is selected from SnCl_4 and TiCl_4 .
 6. The process of claim 3 further comprising the preparation of $\text{CCl}_3\text{CH}_2\text{CCl}_3$ by reacting CCl_4 with vinylidene chloride.
 7. The process of claim 6 wherein said process is conducted in the presence of metal catalyst.
 8. The process of claim 7 wherein the catalyst is cuprous chloride, cupric chloride, or a mixture thereof or cuprous iodide.
 9. A process for the preparation of $\text{CF}_3\text{HC}_2\text{CF}_2\text{Cl}$ comprising reacting $\text{CCl}_3\text{CH}_2\text{CCl}_3$ with HF in the presence of a fluorination catalyst selected from SnCl_4 and TiCl_4 .
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/08263

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C17/23 C07C17/20 C07C17/278 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 539 989 (HOECHST AKTIENGESELLSCHAFT) 5 May 1993 see the whole document ---	1,2
X	EP,A,0 522 639 (SOLVAY (SOCIÉTÉ ANONYME)) 13 January 1993 see the whole document ---	3-9
X	US,A,3 651 019 (M. ASSCHER ET AL.) 21 March 1972 see example 9 -----	3-5

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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